Chapter II

Section A

Graphene-based Composites in Heterogeneous Catalysis

II.A.1 Graphene-based nanocomposites

Owing to the high surface area, excellent conductivity, heterogeneous nature and low manufacturing cost, graphene-based materials have emerged as a new dimension in catalysis.[1] Pristine graphene has two-dimensional structure which easily aggregates due to the π-π interaction between individual graphene layers.[2,3] This stacking of individual layers limits its applications in different fields. Thus it is necessary to surmount graphene's extreme hydrophobic nature which leads to its aggregation. This has been done by the functionalization of graphene nanosheets with other mesoporous/microporous materials.[4] Graphene-based composites have received paramount attention as they are promising candidates for the fabrication of energy conversion devices due to their high energy density.[5] The catalytic efficiency of conventional catalysts largely depends on its surface to volume ratio. In this context, graphene-based catalysts have been found to be extremely useful due to its high surface to volume ratio. This results in an increase in the number of catalytically active sites.

The graphene nanosheets can be blended with different other functional components or materials to form nanocomposites. Most graphene-based composites are composed of two different materials, although ternary composites consisting of more than two materials are also known. The incorporation of a second component could result in the formation of new materials with unique properties due to the synergistic effects of individual components. This provides with a new opportunity for the design and development of new materials and catalysts. Other materials that are used with graphene for the design and development of new functional materials include metal nanoparticles (NPs),[6-8] metal oxides,[9,10] metal-organic framework (MOF),[11,12] polymers,[13,14] bio-materials,[15,16] small organic molecules,[17,18] other nanomaterials like carbon nanotubes and fullerenes,[19,20] mesoporous materials like zeolites, silica, etc.[21-22]

II.A.1.1 Graphene-zeolite composites

Apart from direct functionalization of graphenes with metal and metal oxide NPs, carbonaceous graphene-based composite materials are also used as suitable supports to immobilize metal species for further uses in catalysis.[23] In this context, zeolites have been considered to be a well structured material for blending with graphene.[24] Zeolites are micro-mesoporous and crystalline aluminosilicates with an infinite, three-dimensional framework having large surface area, widely used in catalysis.[5] The catalytic activity of zeolites has been widely used in the petroleum refining industry due to its acid-base properties and hierarchical structure which can be modulated during its synthesis.[25] Moreover, zeolite supported metal species are used in the production of high-octane gasoline and in hydrocracking process.[26] The immobilization of metal NPs onto graphene-zeolite composites could prevent agglomeration of the NPs and accelerate charge transfer. Over the last few years, composite materials from two-dimensional graphene oxide (GO) or reduced GO (rGO) and three-dimensional zeolite have drawn enormous interests because of noticeable morphological changes found in the resulting composites, and primarily they have been used as metal scavengers, membranes or in water purification.[27-31]

II.A.1.2 Graphene-silica composites

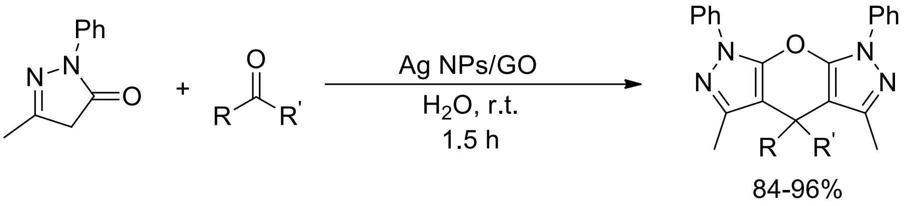
Graphene silica hybrid materials have attracted significant attention because of their remarkable properties.[32,33] Graphene-silica nanocomposite has become one of the superior materials because of their outstanding peoperties.[34] They have been used as adsorbents,[35] catalysts,[36] fillers,[37] and toxic metal ion scavengers.[38] For instance, graphene-silica nanocomposite has been employed for the selective adsorption of Pb^{2+} ions.[39] The most common method for the preparation of graphene-silica nanocomposite has been based on hydrothermal treatments either in presence or absence of surfactants.[22,40] Furthermore, Ag NPs decorated graphene oxide-silica nanocomposite has been synthesized via sol-gel method and employed for the detection of H_2O_2 and glucose.[41]

Chen and co-workers,[42] have synthesized magnetic porous silica-graphene oxide hybrid composites (Fe_3O_4@mSiO_2/GO) and employed it as a potential adsorbent for removal of *p*-nitrophenol from aqueous solutions. R. L. Oliveira described the functionalization of GO surface with organosilanes bearing amine or thiol functionalities and used them as support to immobilize Pd nanoparticles. These new Pd-GO/SiO_2 nanocomposite has been effectively used as a catalyst for the Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions.[43] The synthesis of ultra-small gold nanoparticles immobilized on mesoporous silica coated graphene oxide (GO) nanosheet has been reported by Zhang and his group.[44] This Au/SiO_2/GO nanocomposite could efficiently catalyze the reduction of *p*-nitrophenol.

II.A.1.3 Graphene-metal composites

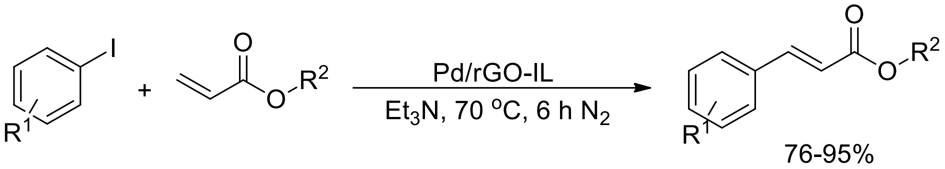
Graphenes or functionalized graphenes decorated with metal NPs is an emerging area in catalysis and other versatile applications. There are different strategies that are employed for the immobilization of metal NPs on the surface of graphene. The most common among them has been based on solution based techniques where the liquid wets the surface. Another approach to construct graphene-metal nanocomposites has been based on chemical functionalization of graphitic surface in order to generate anchoring sites. Graphene oxide (GO) has been generally used for this purpose because the presence of oxygenated groups allows easy functionalization. It has been found that GO is better than its reduced form for the growth of NPs.[45] GO and metal salts or metal precursors are chemically reduced to generate graphene-metal composites.[46,47] An alternate method for the synthesis of metal-graphene composite involves simultaneous reduction of both GO and metals NPs under microwave irradiation.[48,49] Other approaches for the deposition of metal NPs on graphene are electro-deposition,[50] thermal evaporation,[51] photochemical,[52] and solvent-less bulk synthesis.[53] The deposition of metal NPs using this technique depends on several factors like nature of the solvent, type of metal precursor, reducing agents used and the deposition time and temperature. A wide range of noble metal NPs like Au,[54] Pt,[55] Ag,[56] etc., have been immobilized onto graphene surface. Graphene-metal composites based on first row transition metals like Fe,[57] Cu,[58] Ni,[59] and Co,[60] are widely used in catalysis. In addition other reactive metals that are commonly used for preparation of graphene-metal nanocomposites include Pd,[61] Ru,[62] Rh,[63] and Ir.[63] Few examples of graphene-metal nanocomposites that have been used as catalysts are illustrated below.

Dandia and co-workers,[64] have immobilized Ag NPs on the surface of graphene oxide (Ag NPs/GO). The nanocomposite material has been used for the synthesis of pyranopyrazolones in aqueous media. Diverse pyrano[2,3-*c*:6,5-*c*′]dipyrazol-2-ones have been synthesized in 84-96% under ambient conditions (Scheme II.A.1).



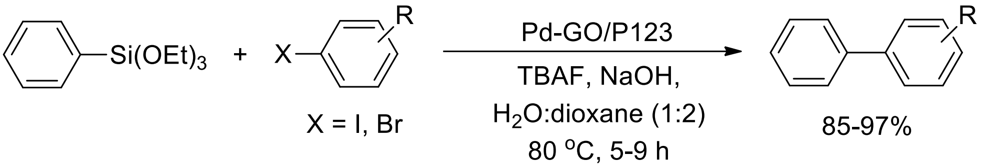
Scheme II.A.1 Ag NPs/GO catalyzed synthesis of pyranopyrazolones.

Palladium nanoparticles immobilized on reduced graphene oxide has been prepared in ionic liquid, [BMIM]PF_6 by phase transfer method (Pd/rGO-IL).[65] The microscopic analysis revealed uniform distribution of Pd NPs on the surface of rGO with average particle size being 2 nm. The nanocomposite catalyst showed excellent activity in Heck coupling reaction (Scheme II.A.2).



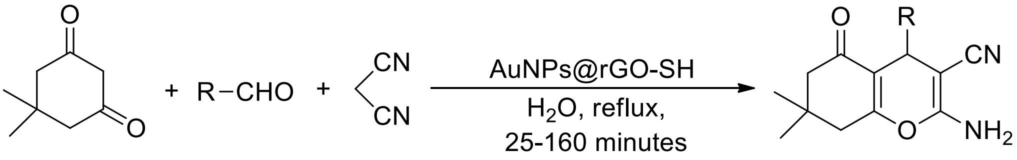
Scheme II.A.2 Pd/rGO-IL catalyzed Heck coupling reaction.

An expedient synthesis of substituted biphenyls via Hiyama cross-coupling reaction (Scheme II.A.3) has been developed by using Pd decorated GO nanosheets under micellar media (Pd-GO/P123). Among the various surfactants, triblock copolymer P123 showed the best results in terms of product yield. The enhanced catalytic activity has been due to the well exfoliation of the graphene oxide layers.[66]



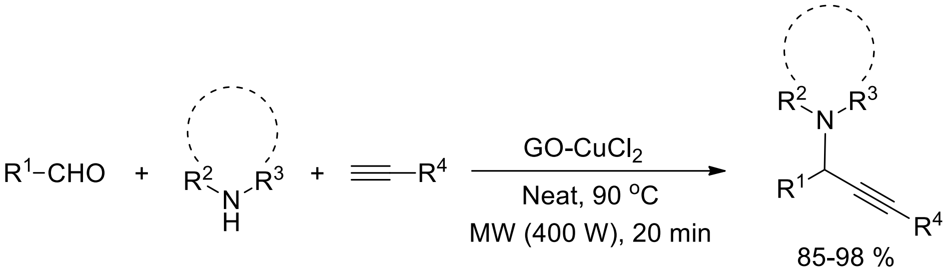
Scheme II.A.3 Hiyama cross-coupling reaction using Pd decorated GO nanosheets.

Gold nanoparticles immobilized on thiol functionalized reduced graphene oxide (AuNPs@rGO-SH) has been prepared and employed for the synthesis of tetrahydro-4*H*-chromenes in aqueous media (Scheme II.A.4). The reaction proceeds through the formation of Knoevenagel intermediate, where gold nanoparticles facilitates polarisation of carbonyl moieties.[67]



Scheme II.A.4 Synthesis of tetrahydro-4*H*-chromenes using AuNPs@rGO-SH.

The synthesis of propargylamines via A^3 coupling reaction has been accomplished by using $CuCl_2$ immobilized on aminopropyl silane functionalized GO (GO-$CuCl_2$) under microwave irradiation.[68] The heterogeneous nature of the catalyst allowed it to be recycled for five runs without significant loss in its activity (Scheme II.A.5).

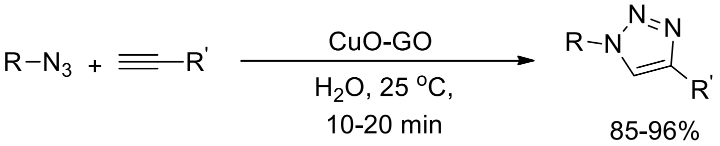


Scheme II.A.5 GO-$CuCl_2$ catalyzed synthesis of propargylamines.

II.A.1.4 Graphene-metal oxide composites

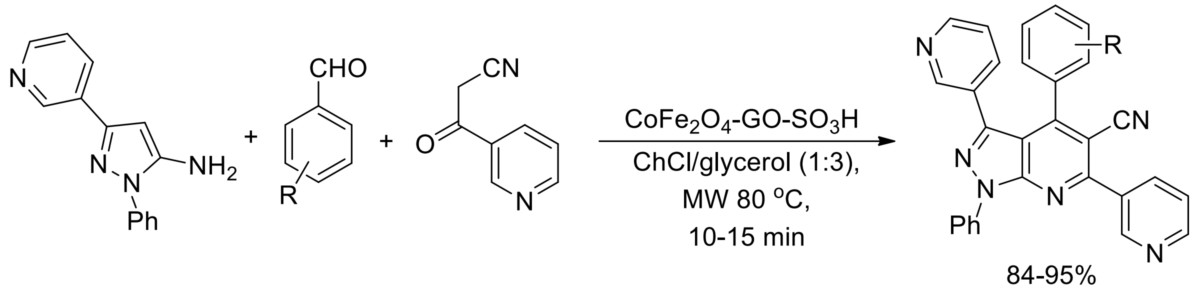
Graphene-metal oxide nanocomposite has been used for energy harvesting, storage devices, nano-optics and in catalysis. Several metal oxide supported graphene nanocomposites have been developed over the last few years. This include TiO_2,[69] MnO_2,[70] SnO_2,[71] Fe_3O_4,[72] Cu_2O,[73] etc. Orth and his group,[74] modified the surface of graphene oxide with thiols for the preparation of sulfur functionalized graphene oxide. The sulfur-functionalized GO has been converted to sorbent by the treatment of TiO_2 or SiO_2. The synthesized sorbent has been used for the removal of Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} as heavy metal ions from aqueous solution in batch method.[75]

Reddy and co-workers,[76] have synthesized 1,4-disubstituted-1,2,3-triazoles by using copper oxide supported graphene oxide (CuO-GO) nanocomposite as a heterogeneous catalyst (Scheme II.A.6) in aqueous media at ambient temperature.



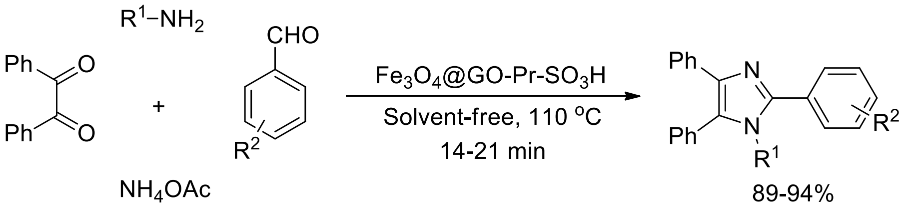
Scheme II.A.6 CuO-GO catalyzed synthesis of 1,4-disubstituted-1,2,3-triazoles.

Magnetic graphene oxide anchored sulfonic acid ($CoFe_2O_4$/GO-SO_3H) has been prepared and used in the synthesis of pyrazolopyridines in deep eutectic solvent under microwave irradiation.[77] A three-component reaction in choline chloride/glycerol as a green solvent afforded the desired products in 84-95% yield (Scheme II.A.7).



Scheme II.A.7 Microwave assisted synthesis of pyrazolopyridines in deep eutectic solvent.

An efficient synthesis of tetrasubstituted imidazoles using sulfonic acid functionalized magnetic graphene oxide (Fe_3O_4@GO-Pr-SO_3H) nanocomposite has been accomplished.[78] The methodology involves a four-component approach using benzil, aromatic aldehydes, primary amines and ammonium acetate (Scheme II.A.8). A wide range of imidazole derivatives has been formed in 89-94% yields.



Scheme II.B.8 Synthesis of imidazoles using magnetic graphene oxide nanocomposite.

II.A.2 Conclusion

The trend towards 'green chemistry' necessitates an entire shift from traditional concepts of process efficiency that largely focuses on chemical yield, to the one that assigns economic value to eliminating waste at the source and avoids use of toxic and/or hazardous substances. Keeping in mind the principles of green chemistry, catalysis via nanomaterials has emerged as a revolutionary way to address multifarious challenges. The fundamental aim of nanocatalysis research is to understand mechanisms at molecular level, and then to design and synthesize catalysts with desired activity. To effect the transition from conventional techniques to modern methods, graphene-based nanomaterials have emerged as an important tool. We believe that novel approaches based on nanomaterials could transform the technology used in modern heterogeneous catalysis.

II.A.3 References

References are given in BIBLIOGRAPHY under Chapter II, Section A.